Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

MIL-101 promotes the efficient aerobic oxidative desulfuration of dibenzothiophenes

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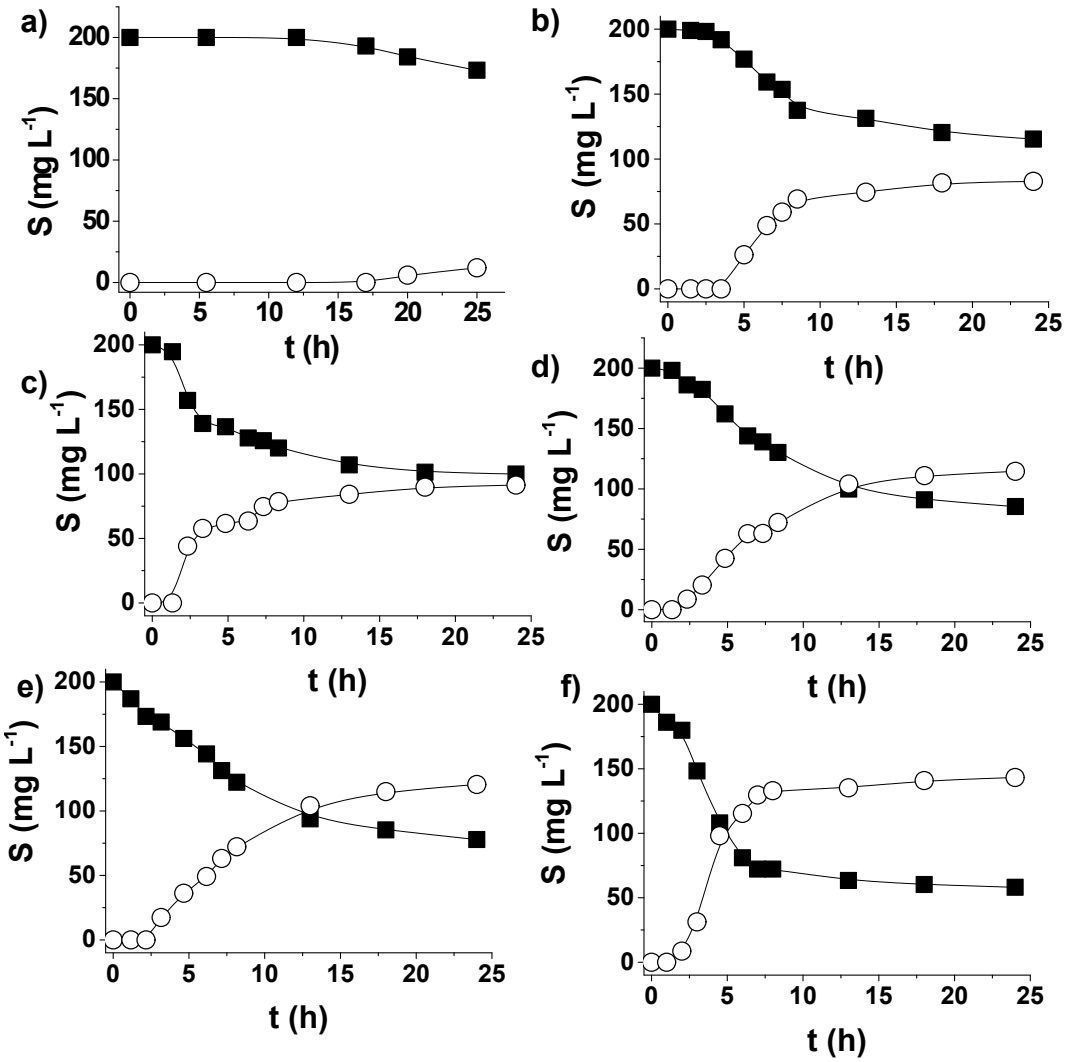

Figure S1 Blank control experiments for the aerobic oxidation of DBT (■) to DBT-Sulfone (Δ) in the absence of catalyst at different reaction temperatures. Legend: a) 120 °C, b) 140 °C, c) 150 °C, d) 160 °C, e) 170 °C and f) 180 °C. Reaction conditions: DBT (1,150 mg L^{-1}), n-dodecane (10 mL), O_2 (1 atm), 120 °C.

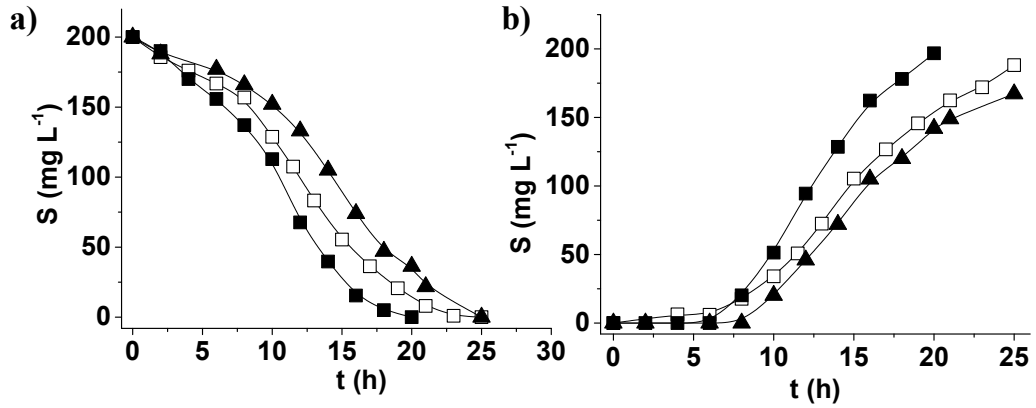

Figure S2 Influence of solvent in the aerobic oxidation of DBT (a) to DBT-S (b) using MIL-101(Cr) as catalyst. Reaction conditions: Catalyst (500 mg L^{-1}), DBT (1,150 mg L^{-1}), solvent (10 mL), O_2 (1 atm), 120 °C. Legend: *n*-decane (■),*n*-dodecane (□),*n*-tetradecane (▲).

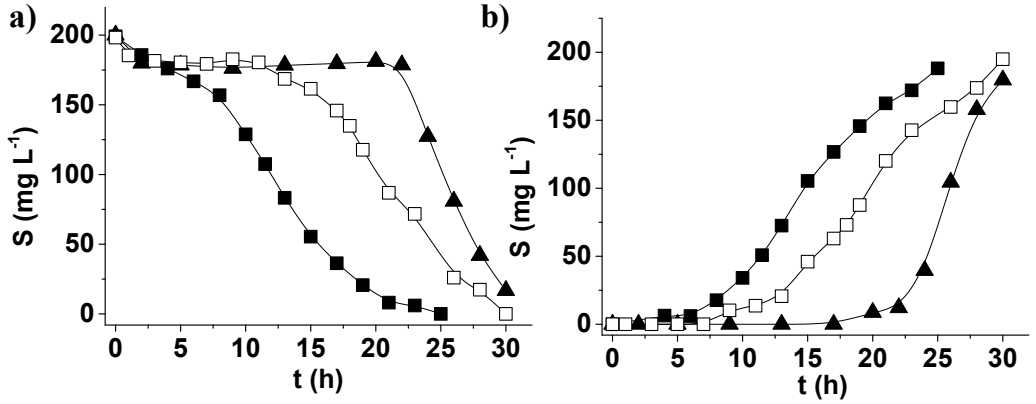

Figure S3 (a) Influence of oxygen partial pressure in the aerobic oxidation of DBT to DBT-Sulfone; (b) Relationship between the initial reaction rate of DBT degradation and the partial oxygen pressure. Reaction conditions: Catalyst (500 mg L^{-1}), DBT (1,150 mg L^{-1}), dodecane (10 mL), reaction atmosphere (1 atm), 120 °C. Legend: O_2 (■),air (□), Ar for 23 h and then O_2 atmosphere (▲).

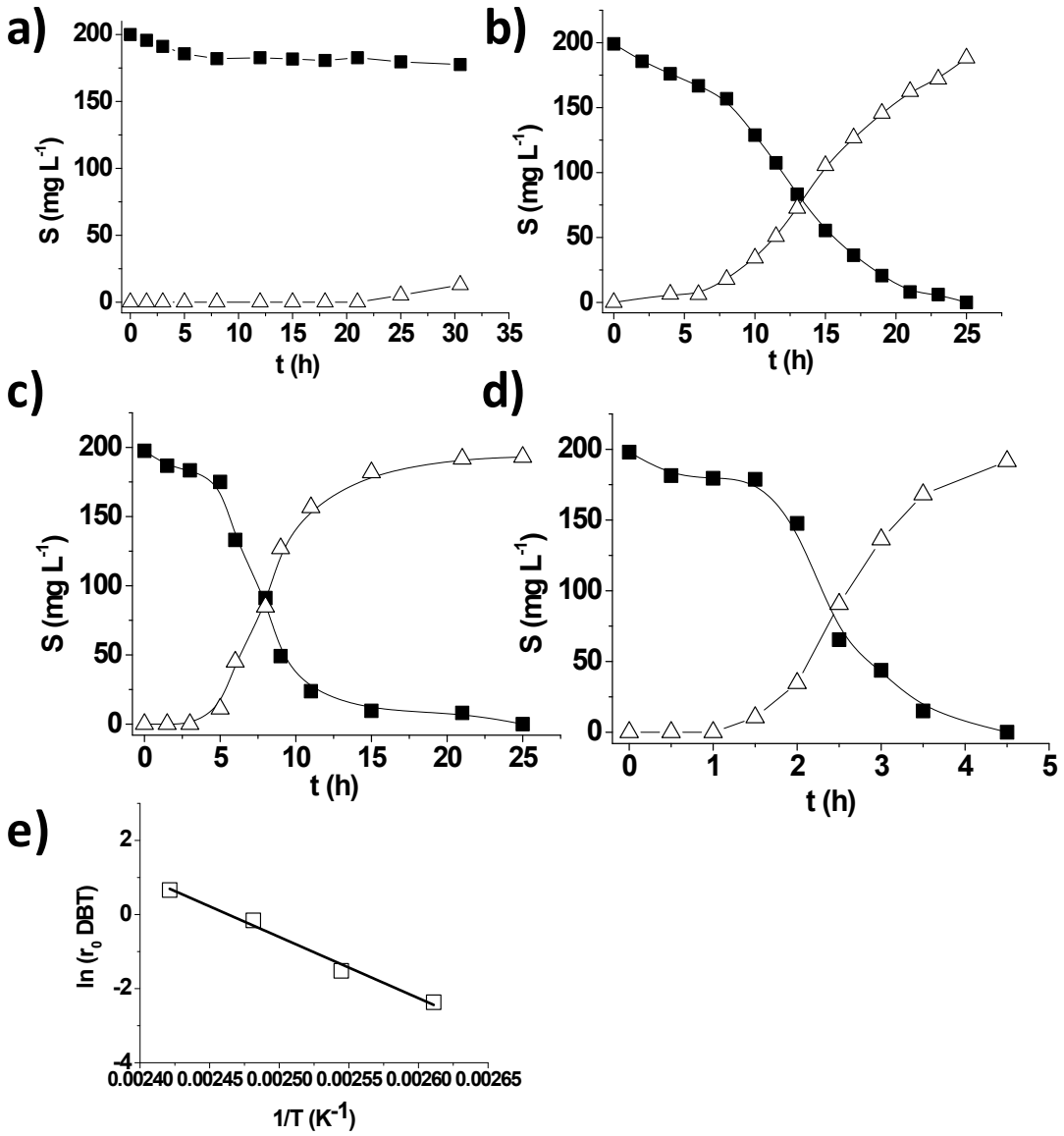

Figure S4 Influence of the reaction temperature namely 110 °C (a), 120 °C (b), 130 °C (c) or 140 °C (d) and Arrhenius plot (e) in the aerobic oxidation of DBT (■) to DBT-Sulfone (Δ) using MIL-101(Cr) as catalyst. Reaction conditions: Catalyst (500 mg L^{-1}), DBT (1,150 mg L^{-1}), *n*-dodecane (10 mL), O_2 (1 atm), T (as indicated).

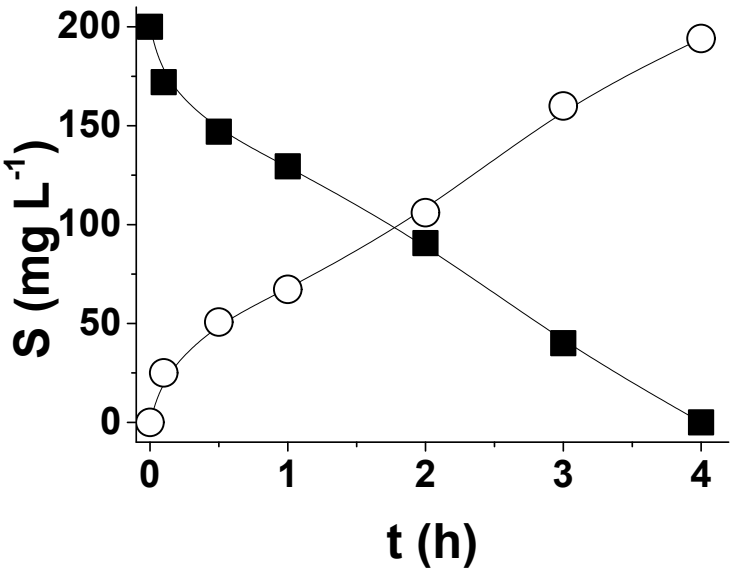

Figure S5 Aerobic oxidation of DBT (■) to DBT-S (○) using 10 mg of MIL-101(Cr) as catalyst. Reaction conditions: Catalyst (1,000 mg L^{-1}), DBT (1,150 mg L^{-1}), solvent (10 mL), O_2 (1 atm), 140 °C.

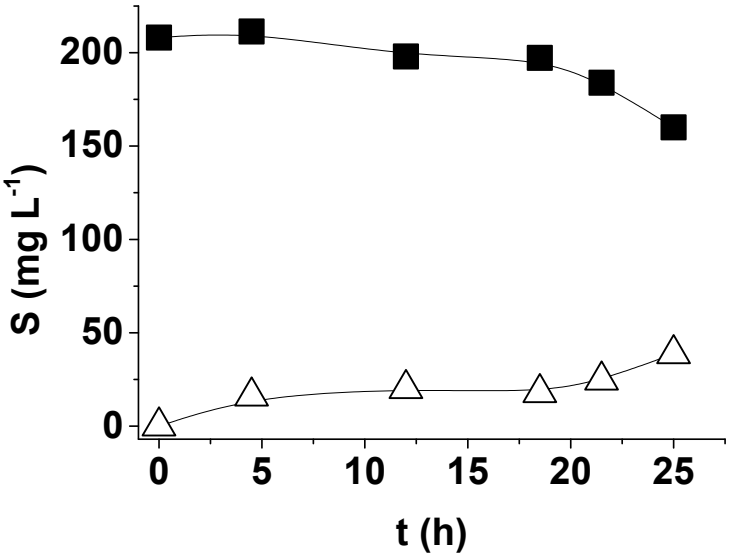

Figure S6 Blank control experiment for the homogeneous aerobic oxidation of DBT with O_2 in the presence of Cr(III) acetate hydroxide as homogeneous catalyst. Reaction conditions: Chromium(III) acetate hydroxyde (0.6 mg L^{-1} as Cr^{3+}), DBT (1,150 mg L^{-1}), *n*-dodecane (10 mL), O_2 (1 atm), 120 °C.

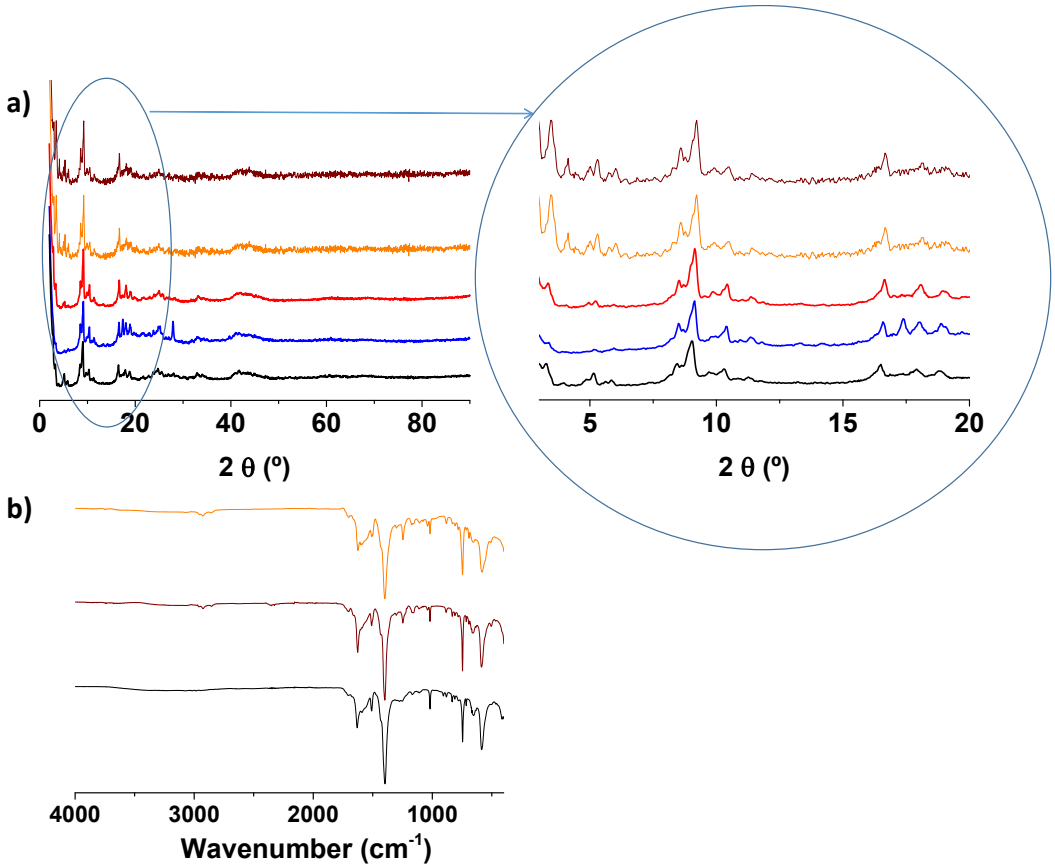

Figure S7 XRD (a) and ATR-FT-IR of fresh and used MIL-101(Cr) samples. Legend for MIL-101(Cr) samples: fresh (black), used and non-whased (blue), one use (red), three uses (orange) and five uses (brown) and washed MIL-101(Cr). Reaction conditions of the used MIL-101(Cr) sample: Catalyst (500 mg L^{-1}), DBT (1,150 mg L^{-1}), *n*-dodecane (100 mL), O_2 (1 atm), T (120 °C).

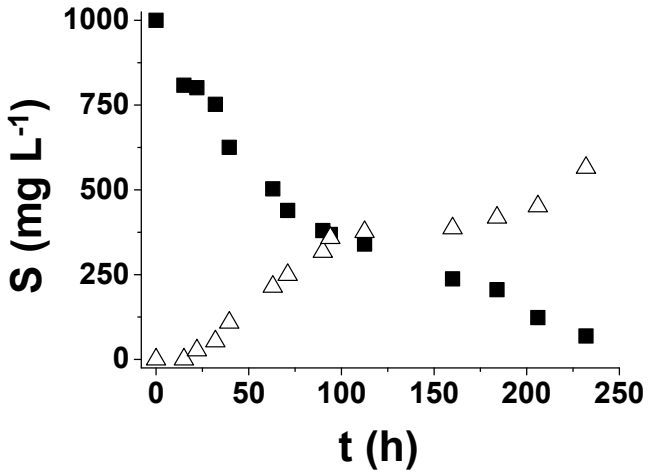

Figure S8 Productivity test for the aerobic oxidation of DBT (■) to DBT-Sulfone (Δ) using MIL-101(Cr) as catalyst. Reaction conditions: Catalyst (10 mg L^{-1}), DBT (5,750 mg L^{-1}), *n*-dodecane (10 mL), O_2 (1 atm), 120 °C.

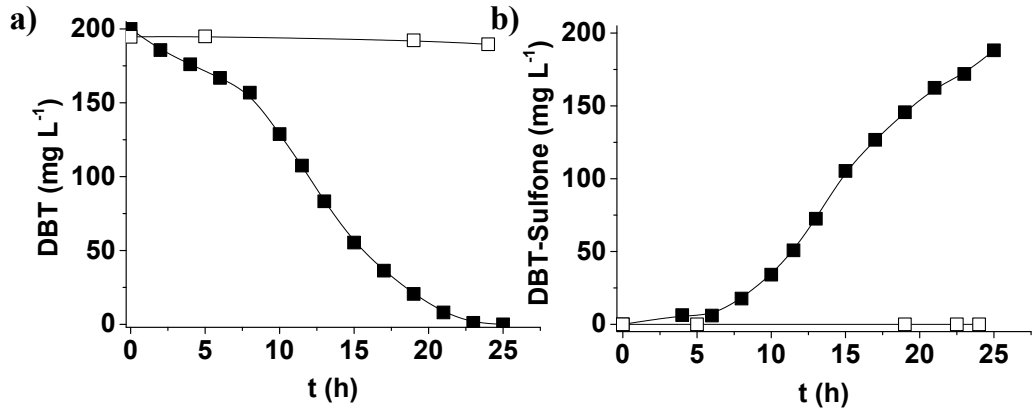

Figure S9 Aerobic oxidation of DBT (a) to DBT-Sulfone (b) in the absence (■) and in the presence of *p*-benzoquinone (□) as selective $O_2^{\cdot-}$/HOO· radical scavenger using MIL-101(Cr) as catalyst. Reaction conditions: Catalyst (500 mg L^{-1}), DBT (1,150 mg L^{-1}), *p*-benzoquinone (20 mol % respect to DBT), *n*-dodecane (10 mL), O_2 (1 atm), 120 °C,

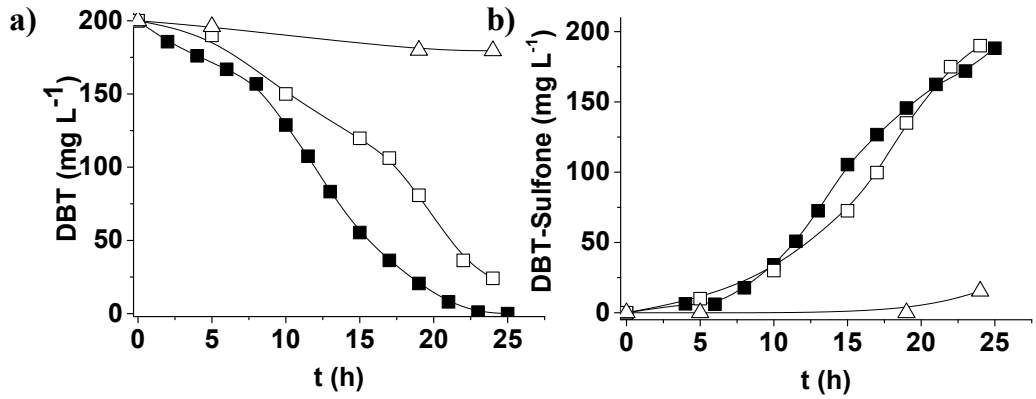

Figure S10 Aerobic oxidation of DBT (a) to DBT-Sulfone (b) using MIL-101(Cr) as heterogeneous catalyst or using TBHP (□) or benzoyl peroxide (Δ) as homogeneous catalyst. Reaction conditions: MIL-101(Cr) (500 mg L^{-1}), TBHP or benzoyl peroxide (20 mol % respect to DBT), DBT (1,150 mg L^{-1}), *n*-dodecane (10 mL), O_2 (1 atm), 120 °C.

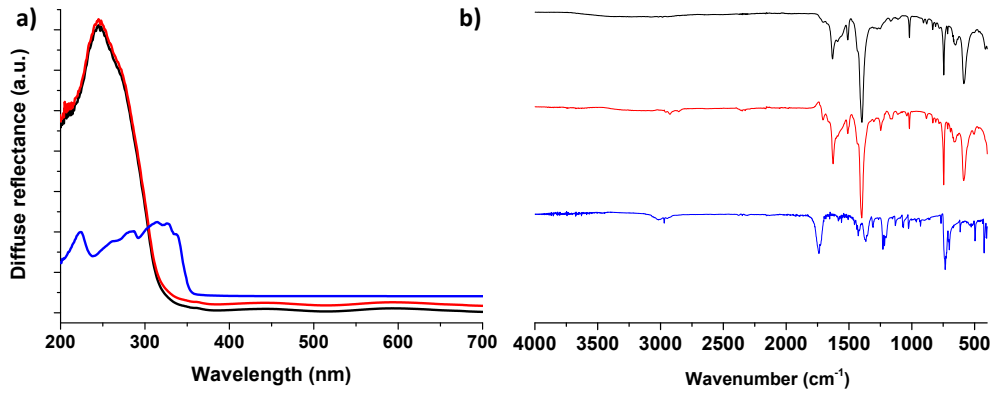

Figure S11 (a) Diffuse reflectance UV-vis absorption (a) and ATR-FT-IR (b) spectra of MIL-101(Cr) (black line), DBT (blue line) and MIL-101(Cr)+adsorbed DBT (red line). Adsorption conditions: MIL-101(Cr) (25 mg), DBT (1,150 mg L^{-1}), *n*-dodecane (50 mL), room temperature, 24 h.

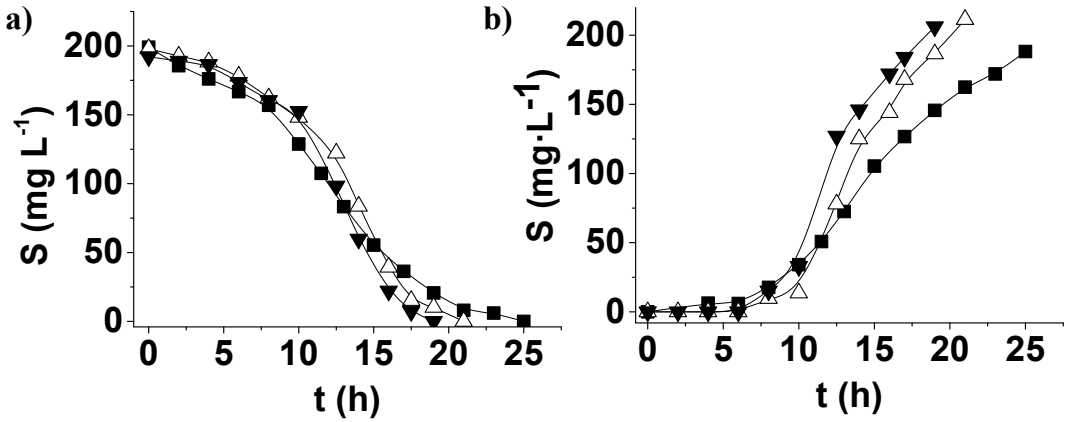

Figure S12 Aerobic oxidation of DBT, 4-methyl DBT and 4,6-dimethyl DBT to their corresponding sulfones in the presence of MIL-101(Cr) as catalyst. Reaction conditions: Catalyst (500 mg L^{-1}), substrate (200 mg L^{-1} as S), *n*-dodecane (10 mL), O_2 (1 atm), 120 °C. Legend (a): DBT (■), 4-methylDBT (Δ), 4,6-dimethylDBT (▼); Legend (b): DBT-Sulfone (■), 4-methyl DBT-Sulfone (Δ), 4,6-dimethylDBT Sulfone (▼).

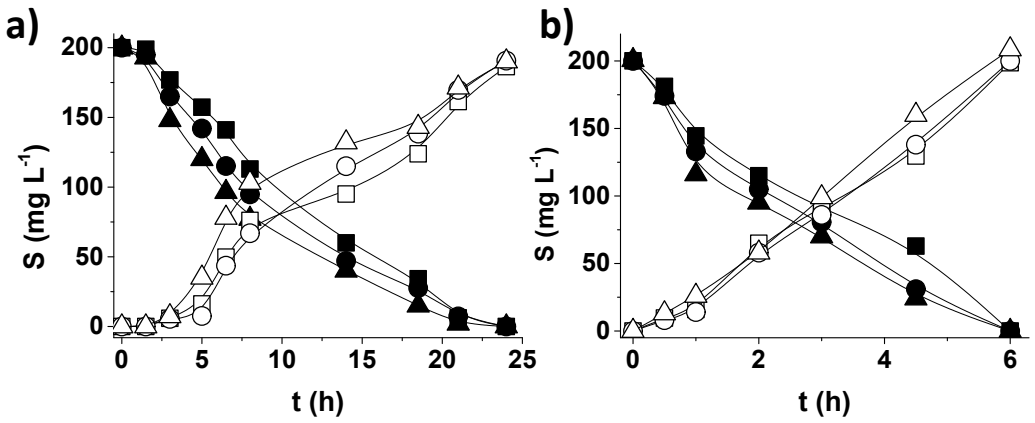

Figure S13 Aerobic oxidation of DBT, 4-methyl DBT and 4,6-dimethyl DBT in a multicomponent system to their corresponding sulfones at 120 °C (a) or 140 °C (b) in the presence of MIL-101(Cr) as catalyst. Reaction conditions: Catalyst (500 mg L^{-1}), substrate (200 mg L^{-1} as S each component), *n*-dodecane (10 mL), O_2 (1 atm), T as indicated. Legend (a): DBT (■), 4-methylDBT (●), 4,6-dimethylDBT (▲); Legend (b): DBT-Sulfone (□), 4-methyl DBT-Sulfone (○), 4,6-dimethylDBT Sulfone (Δ).

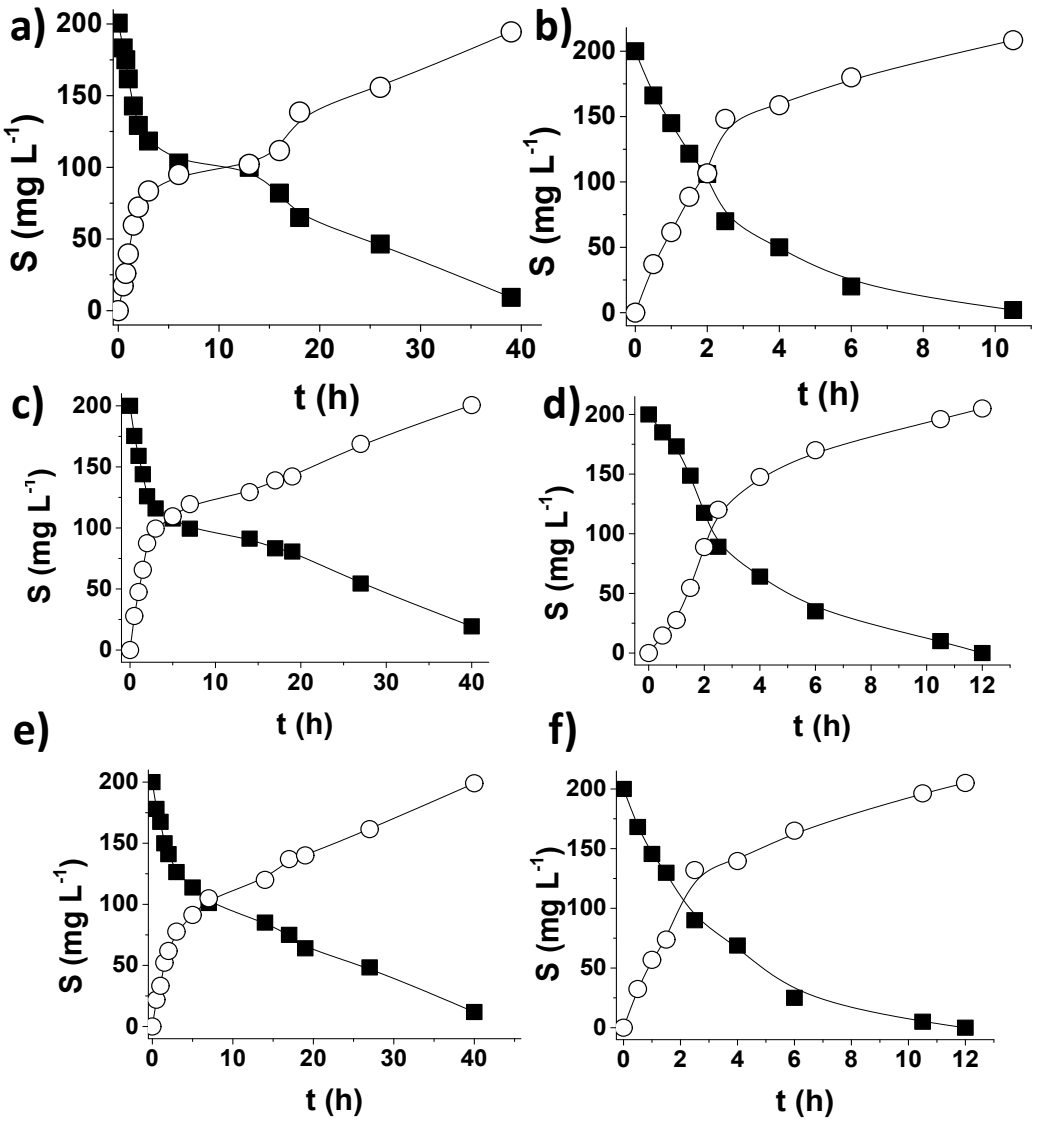

Figure S14 Aerobic oxidation of DBT (a, b), 4-methyl DBT (c, d) and 4,6-dimethyl DBT (e, f) to their corresponding sulfones at 120 °C (a, c, d) or 140 °C (b, d, f) in the presence of MIL-101(Cr) as catalyst. Reaction conditions: Catalyst (500 mg L^{-1}), substrate (200 mg L^{-1} as S), commercial diesel (10 mL), O_2 (1 atm), T as indicated.